COMPLEX CARBOHYDRATES IN FOODS

The Report of the British Nutrition Foundation's Task Force

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COMPLEX CARBOHYDRATES IN FOODS

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TERMS OF REFERENCE

1. To review the nutritional attributes of complex carbohydrates (primarily in foods) in relation to current dietary advice to the population to increase the consumption of such foods. Complex carbohydrates for the purpose of the remit of the Task Force include all polysaccharides containing 20 or more monosaccharide residues. Reference to polysaccharides less than 20 monosaccharide units are made where appropriate.
2. To prepare a report and, should it see fit, draw conclusions and identify areas for future research.

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FOREWORD

The British Nutrition Foundation organises independent 'Task Forces' to review, analyse, and report in depth upon specific areas of interest and importance in the field of human nutrition.

These expert committees consist of acknowledged specialists and operate completely independently of the Foundation.

The *Complex Carbohydrates in Foods* Task Force has reviewed and discussed much published information. This report summarises the deliberations and findings of the Task Force, and gives its conclusions and recommendations.

I am most grateful to the members of the Task Force who have contributed their time and expertise so generously. My sincere thanks also go to the Secretariat for their excellent support.

Professor Dame Barbara Clayton
Chairman of the Task Force

CONTENTS

CHAPTER 1
INTRODUCTION

The value of 'fibre' in the diet was even recognised by the Greeks. Hippocrates, in the fourth century BC, commented 'To the human body it makes a great difference whether the bread be made of fine flour or coarse, whether of the wheat with the bran or the wheat without the bran'.

In the nineteenth century, Graham and Kellogg in the United States and Allinson in Britain tried to draw attention to the importance of 'fibre' in the diet, all with limited success.

Modern interest in carbohydrates and health began with Surgeon Captain Cleave's exposition of 'The Saccharine Disease'. Under this title, Cleave (1966) brought together a variety of conditions characteristic of the Western World which he thought were due to consumption of refined carbohydrates. This hypothesis was then developed by Burkitt and Trowell (1975) who suggested that it was the diets of Africans which protected them from most of the chronic non-infective diseases characteristic of Western culture. They suggested that many Western diseases were due to lack of 'fibre' in the diet rather than to the direct ill-effects of refined or 'fibre'-depleted foods. At about the same time, Painter (1975) presented his evidence that diverticular disease could be successfully treated with bran. A full account of the contribution made by the early 'pioneers' of the 'fibre' hypothesis has been given by Trowell (1985).

Their ideas stimulated much research, and in 1980, The Royal College of Physicians published a report on 'Medical Aspects of Dietary Fibre' (Royal College of Physicians, 1980). The RCP committee concluded that 'On present evidence, we think it highly probable, though not fully proved and possibly not susceptible of rigid proof, that increasing the proportion of "dietary fibre" in the diet in Western countries would be nutritionally desirable'. They highlighted two reasons why their conclusions and recommendations had to be tentative:

(i) the diversity of compounds which are loosely grouped together as dietary 'fibre'.
(ii) the imprecision of the epidemiological comparisons between populations consuming a high-'fibre' diet and those consuming a low-'fibre' diet.

The Report recommended that further research was required before any detailed dietary recommendations could be made to the general public.

In 1988, the British Nutrition Foundation decided to convene this independent Task Force, to see what progress had been made. Complex carbohydrates, defined as starches plus non-starch polysaccharides, rather than 'fibre', was chosen as the title and subject of the Report for various reasons:

(i) The US Senate Select Committee on Nutrition and Human Needs (1977) had concluded that the intake of complex carbohydrates should be increased as one of its Nutritional Goals.
(ii) The DHSS Committee on Medical Aspects of Food Policy (1984) had recommended that a reduction in total fat in the diet could be achieved by an increased consumption of 'fibre-rich' carbohydrates (eg bread, cereals, fruit, vegetables).
(iii) It had recently been shown that some forms of starch could resist digestion in the small intestine (Englyst *et al.*, 1987a). These resistant starches could act as

substrates for fermentation in the colon and thus exhibit similar properties to the non-starch polysaccharides.

The variety of chemical entities that constituted what was colloquially called dietary 'fibre' needed definition and it was felt that a greater understanding could be achieved if the effects of the starches, the resistant starches and the non-starch polysaccharides were examined together.

Increasing consumer awareness of the relationship between diet and health has led to demands for more widespread nutrition labelling. How 'fibre' should appear on the label, which method of analysis should be used and whether one single value is appropriate are all current issues which are addressed in the Report. The potential ability of complex carbohydrates to prevent, or alleviate various diseases is also relevant to the validity of health claims which are starting to appear on food products.

The Report begins by classifying the different compounds that make up complex carbohydrates and describes where they are found in the UK diet (Chapters 2 and 3). It goes on to look at how the form and physical properties of both starches and non-starch polysaccharides determine their effects in the small intestine (Chapters 4 and 5) and the subsequent outcome on the digestion and absorption of macronutrients and micronutrients (Chapters 6 and 7). The effects of complex carbohydrates on the glycaemic response are considered in Chapter 10. The interaction of complex carbohydrates that pass into the large intestine with bacteria is discussed in Chapter 8, and their dietary energy values are considered in Chapter 9.

The role of complex carbohydrates in the aetiology of a number of diseases is critically reviewed (Chapters 11 to 19) and the conclusions reached are pertinent to whether starches and non-starch polysaccharides are essential components of the diet. If so, how much should the diet provide and can a recommendation applicable to various groups of the population be determined? The various arguments for and against quantitative recommendations are outlined in Chapter 20 and labelling implications are discussed in Chapter 21.

The popular term, dietary 'fibre', previously defined as 'any substance of plant origin which is undigested by human alimentary enzymes' (Trowell *et al.*, 1972), has been avoided as far as possible in the Report. This Task Force felt that it would be helpful to identify the particular polysaccharide responsible for the observed effects, in the hope that some clarification of the confused state of the literature could be achieved.

This Report provides an objective and timely assessment of the current state of knowledge in what is an exciting area. It points the way ahead to the further research that is required and, more importantly, indicates how this can be done most effectively.

CHAPTER 2
CHEMISTRY OF COMPLEX CARBOHYDRATES AND THEIR ORGANISATION IN FOODS

2.1 INTRODUCTION

This chapter provides an introduction to the chemical and physical structure of the complex carbohydrates as a background to the later chapters on physiological and nutritional properties of this group of substances. In preparing the chapter much use has been made of a number of detailed reviews, and reference to these is essential for the detailed discussion of the primary literature on these substances.

2.1.1 Definition of complex carbohydrates

The term 'complex carbohydrates' was used in the McGovern report (US Senate Select Committee on Nutrition & Human Needs, 1977) without formal definition. In the context of the report, it was used to distinguish the simple sugars from the polysaccharides. This definition is the one most suitable for use in the context of the work of this Task Force so that 'complex carbohydrates' is effectively a synonym for polysaccharides and a reasonable delineation of polysaccharides would be all carbohydrate polymers that contain *twenty* or more monosaccharide residues.

The simple carbohydrates on this basis will include the mono, di-, tri-, and tetrasaccharides and sugar alcohols present in food and other oligosaccharides containing up to 19 residues. This somewhat arbitrary definition is a convenient one pragmatically, because oligosaccharides with more than four residues are rare in foods, except as fragments of polysaccharides produced by enzymatic or acid hydrolysis, eg they are present in starch hydrolysates (glucose syrups). It is also a definition which has some basis in terms of physical structure since some form of tertiary structure has usually developed with a molecule of this size.

The complex carbohydrates, therefore, display a wide range of chemical and physical properties. Furthermore many of them are organised into physical structures in foods, for example, starch granules and cell wall structures, that confer other properties on them.

It is therefore not possible to discuss them as an entity since they share a limited range of common properties, principally that of being polysaccharides and not simple sugars. In general they are insoluble in aqueous alcohols at about 80% v/v but this is not an absolute distinction since many fructans and glucofructans and some arabinans are soluble in aqueous ethanol.

2.1.2 Terminology of complex carbohydrates

Formal rules for the systematic terminology of polysaccharides have yet to be established but one can forecast that such nomenclature will be very complex and too unwieldy for general use. There is, however, a reasonable series of generic terms that can be systematised and these will be used to discuss general classes of polysaccharide structures:

Homopolysaccharides are polysaccharides containing only one monosaccharide or

uronic acid residue. They form the largest proportion of polysaccharides. In a strict sense, it is probable that pure homopolysaccharides are uncommon; the terminology relates to polysaccharides that are virtually all composed of only one type of residue.

Homopolysaccharides are named using the prefix of the constituent residue and the suffix *an* - thus starch, glycogen and cellulose are glucans, inulin is a fructan.

Heteropolysaccharides are polysaccharides containing more than one monosaccharide or uronic acid residue.

Heteropolysaccharides are named using the substituent side chains as the prefix followed by the backbone constituent with the suffix *an*. Thus, xyloglucans have a glucose backbone with xylose side chains, arabinoxylans have a xylose backbone with arabinose side chains, galactomannans have a mannose backbone with galactose side chains, uronans are uronic acid polymers.

Glycan is the general systematic terminology for polysaccharides.

2.1.3 Classification of complex carbohydrates

It is possible to construct a number of different systems for classifying the complex carbohydrates (Table 2.1). None of the systems is entirely satisfactory in that the boundaries between categories are not absolute, either structurally or functionally, nor are the boundaries susceptible to precise analytical demarcation. This is due to the fact that the range of reactions that various polysaccharides undergo is limited and non-specific. Many reactions are common to one or more, and usually several, polysaccharides.

The majority of the complex carbohydrates in the human diet are derived from foods of plant origin and classification according to the major functional role in plants is a convenient basis for discussion of their chemistry, properties and organisation (Selvendran, 1984).

Polysaccharide food additives of plant origin are widely used in foods. Many of these are of cell wall origin and closely related to the analogous cell wall polysaccharides.

They are, however, present in foods as the isolated polysaccharides with, or without, further chemical modification and therefore are considered separately.

A range of polysaccharides is present in animal tissues. Animal foods therefore contribute small amounts of complex carbohydrates to the average UK diet. There are no reliable estimates, but the amounts may reach significant levels in extreme carnivorous diets. These polysaccharides, although quantitatively insignificant, are available in large quantities as by-products of meat, fish and, especially, crustacea processing. They have been suggested as possible food additives because of their specific properties.

The complex carbohydrates are therefore discussed under the following headings:

- Storage Polysaccharides
- Cell Wall Polysaccharides
- Isolated Polysaccharides
  - i) naturally occurring
  - ii) polysaccharide food additives
- Polysaccharides of Animal Origin

Within each category, structure and chemical properties are considered.

2.2 STORAGE POLY-SACCHARIDES

The major storage polysaccharides in foods of plant origin are the starches, although a range of fructans is found in many roots, tubers, and some cereal seeds. Some members of the legume family have variously substituted mannans as the major storage polysaccharide, as do some nuts. In virtually all human diets, starches form

Table 2.1 Alternative classifications of food polysaccharides

Role in the plant/food	Types of polysaccharides	Analytical classification	Site of digestion	Products of digestion	Physiological classification
Storage polysaccharides	Starch amylose amylopectin	α-glucans	Small intestine (enzymatic)	Mono and di saccharides	Available carbohydrates
	Fructans				
	Galactomannans	Non α-glucans			
Structural components of the plant cell walls	Non-cellulosic Pectins Hemicellulose Cellulose	Non-starch polysaccharides	Large intestine (Microbial)	Short chain fatty-acids: acetate propionate butyrate	Unavailable carbohydrates
Isolated polysaccharides Naturally occurring	Gums Mucilages Pectin			Carbon dioxide, hydrogen, methane	
Polysaccharide food additives	Gums Algal polysaccharides Modified celluloses Modified starches				

the major, and often only, storage polysaccharides. In some diets, where tubers form a major part of the diet, the intakes of other storage polysaccharides may be significant.

Glycogen, the storage polysaccharide in animal tissues is rapidly hydrolysed and metabolised *post-mortem*, and is not a significant contribution to complex carbohydrate intakes unless the liver is consumed fresh and raw. In practical nutritional terms, it is therefore only necessary to discuss the storage polysaccharides of plant origin.

2.2.1 Starches

It is preferable to use the plural form because a number of distinct chemical structures and physical levels of organisation are seen. This usage emphasises the fact that starch cannot be considered as a homogeneous component of foods and the diet.

2.2.1.1 Structure

The starches are α-glucans, containing both 1-4 and 1-6 linkages. Two major structural types are present in most foods: Amylose is a linear 1-4 molecule and amylopectin is a branched molecule with both 1-4 and 1-6 linkages. Many food starches contain some intermediary structures where an essentially linear 1-4 molecule contains some 1-6 linkages. The starches are characteristically polydisperse and most preparations isolated using mild conditions contain a range of molecular sizes.

Amyloses are the minor component of starch (15-20%) and typically have molecular weights up to around 60,000 Daltons. The stereochemistry of the 1-4 α-linkage confers a helical conformation on amylose. The interior of the coil can be occupied to form inclusion compounds with, for example, monoglycerides and notably iodine to give the very delicate and characteristic blue colour of the iodine-starch reaction.

Amylopectins are the major components of starch. They are usually larger molecules

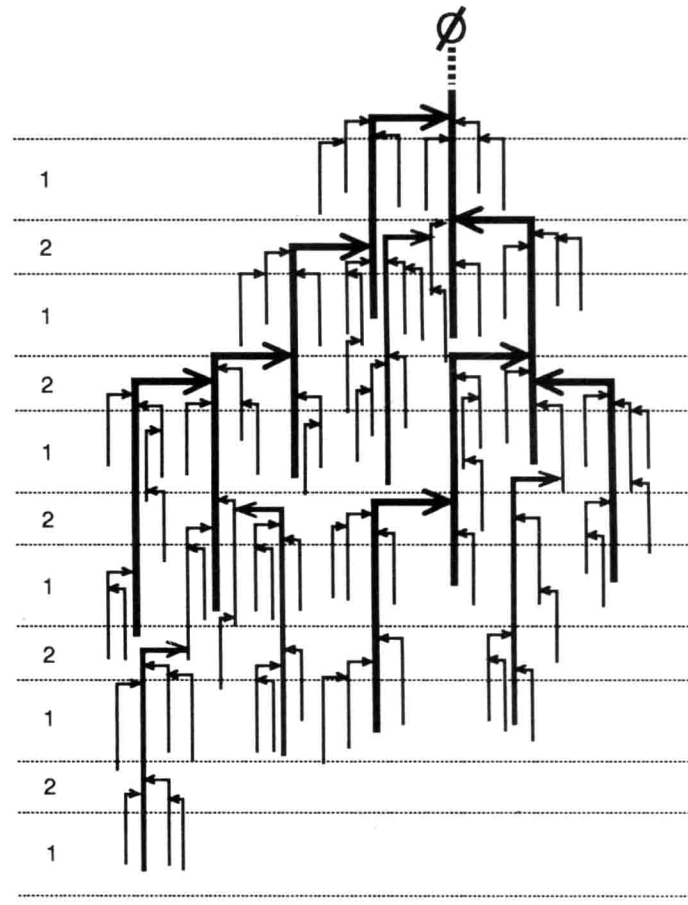

Figure 2.1 Structure of amylopectin. 1 minimal branching region; 2 maximum branching region.

with molecular weights of over 1 million Daltons (greater than 10,000 glucose residues). They have a considerably more complex structure and the details of this fine structure are still the subject of debate and research. Most recent observations give general support to the tree-link structure (Figure 2.1) (French, 1972; Würsch, 1990). The side chains of the molecule are 1-4 linked and are therefore potential helical structures within the steric constraints of the molecule as a whole.

2.2.1.2 Properties

2.2.1.2.1 Effect of heating

The starches are characteristically insoluble in cold water, but disperse on heating to produce colloidal sols. The linear amylose molecules readily associate and form hydrogen bonds. This produces precipitates from dilute solutions and gels from more concentrated ones; a process known as retrogradation. Amylopectins associate less readily, but retrogradation occurs when the side chains associate.

2.2.1.2.2 Effect of group substitution

The hydroxyl groups of the molecule can be substituted with methoxy, acetyl and related constituents to produce a range of modified starches. Organic ester and phosphate ester can also be generated and these are also used as modified starches. Some native starches contain phosphate groups. The modified starches exhibit

a range of physical properties; for this reason they are wholly used to control or modify the textural characteristics of food products (Kearsley and Sicard, 1989).

2.2.1.2.3 Acid hydrolysis

The starches are readily hydrolysed by acids and enzymes. Acid hydrolysis, combined with selective enzymatic hydrolysis, is used to produce a range of food products, ranging from starches which have been partially depolymerised to glucose syrups where extensive hydrolysis has taken place. The extent of hydrolysis can be closely controlled to produce hydrolysates with specific physical properties and levels of sweetness for use in food products.

Acid hydrolysis involves the addition of water to the glucosidic bond, the attack being generally random. The mechanism of acid hydrolysis is such that the intermediates could rearrange to produce furfural derivatives, be released as free glucose, or recombine to form dextrins. Under strong acid conditions, the dehydration of the intermediate to furfural is favoured. Dilute hydrolysis and low initial concentrations of starch favour the formation of free glucose.

Acid hydrolysis forms the basis of many methods for measuring starch in the absence of other hydrolysable polysaccharides. Theoretical yields of glucose are achieved with 1M sulphuric acid with initial concentrations of starch around 100–200 mg/litre (Southgate, 1976). In the presence of other polysaccharides, a glucose specific method, such as glucose oxidase is required for accurate measurements. This is not adequate if β-glucans, branched 1-2 and 1-3 polymers as found in many cereals especially oats and barley, are present. Most specific procedures for starch rely on enzymatic hydrolysis.

2.2.1.2.4 Enzymatic hydrolysis

A number of different α-glucosidases (α glucan hydrolysases EC 3.2.1.n) are known. They are present in salivary and pancreatic secretions of many mammals and also produced by many fungi, bacteria and protozoa. They were originally classified into α and β amylases according to the basis of their mode of attack on the starch molecule (see Figure 2.2).

α amylases (1, 4 α-D-Glucan-glucanohydrolases, EC 3.2.1.1.) are endoenzymes which hydrolyse the 1-4α glucosidic bonds at random producing a range of fragments. The action terminates at 1,6 linkages and therefore, the hydrolysis products of amylopectin include α-limit dextrins and isomaltoses. *In vivo*, these are hydrolysed further by the isomaltases (EC 3.2.1.10.) in the brush borders of the mucosal cells.

β amylases (1, 4 β-D-Glucan maltohydrolases EC 3.2.1.2) hydrolyse alternate α-1, 4 linkages to give maltose. The hydrolysis products from *amylopectin* include β-limit dextrins and *isomaltoses*. A number of *glucoamylases* (1, 4 α-D-Glucan glucano hydrolases, EC 3.2.1.3) are found in fungi and other microorganisms. These are exoenzymes and hydrolyse the polymers from the reducing ends producing glucose. Some 1,6 activity is usually present and the enzymes can give virtually complete hydrolysis of starches provided that the material is free from retrograded amylose.

2.2.1.2.5 Factors affecting hydrolysis

In vitro studies of the kinetics of hydrolysis of starch show differences in susceptibility to α-amylase hydrolysis. Both the rate and extent of hydrolysis show differences that are dependent on the plant source of the starch and physical properties such as particle size. A major factor in determining both rate and extent of hydrolysis is the state of the granule, and particularly the type of physical treatment that the starch has received (Würsch, 1990). These are particularly important in determining the behaviour of starch physiologically because most starchy foods are consumed after some kind of heat treatment.

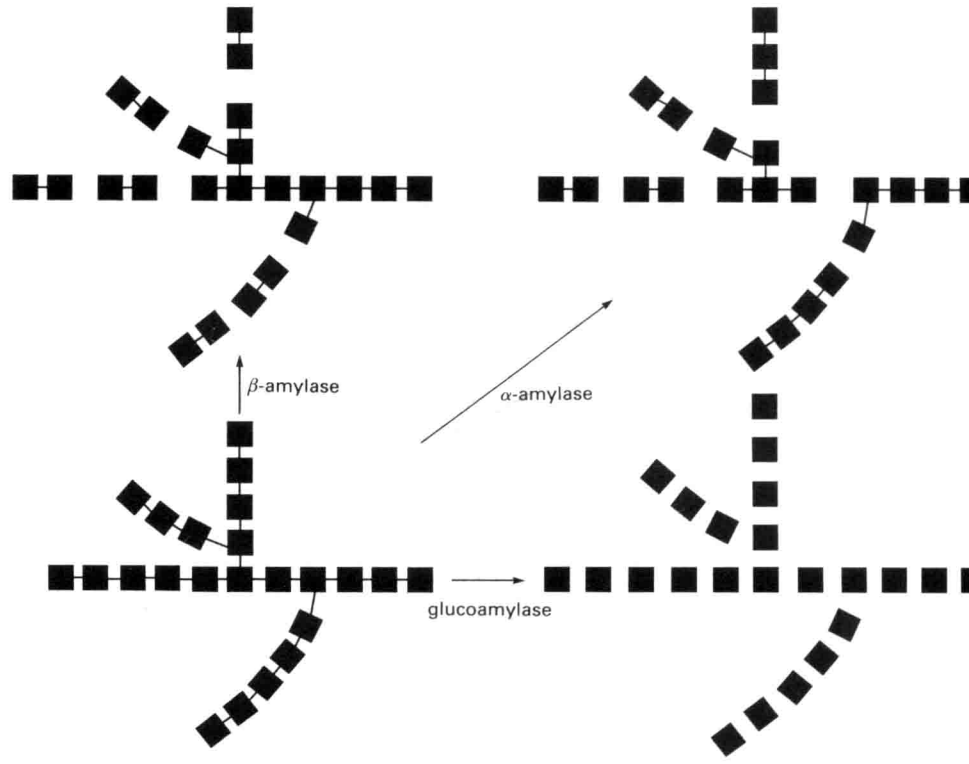

Figure 2.2 Enzymatic hydrolysis of starch. α-amylases hydrolyse α1-4 glucosidic bonds at random. They terminate at α1-6 linkages. β-amylases hydrolyse alternate α1-4 linkages. Glycoamylases hydrolyse α1-4 and α1-6 linkages sequentially.

The detailed organisation of the starch granule is still an active topic for research and most of the current knowledge comes from studies of wheat and other cereal starch granules. The native granule shows a characteristic x-ray diffraction pattern indicating an element of crystallinity in its organisation. The native granule has a phospholipid coat that acts as an initial barrier to enzymatic attack. On treatment with heat in an aqueous environment the granule absorbs water and swells, and when the granule ruptures amylose is leached out, but the x-ray pattern is still evident indicating that the amylopectin plays a major role in the actual structure of the granule.

Most heat treated foods contain a range of granular structures ranging from relatively intact granules such as those in the crust of bread, to starches where the granular structure has virtually disappeared such as those in the breadcrumb. In relatively few foods (eg the unripe banana), the granule is consumed in its native crystalline state.

Englyst *et al.* (1982) has developed a scheme for classifying the starch in foods according to its physical state in relation to susceptibility to enzymatic hydrolysis *in vitro* and its imputed hydrolysis *in vivo* (see Chapter 4 and Table 4.1).

However, at the present time, the range of factors that determine starch hydrolysis *in vivo* cannot be predicted from chemical and physical analysis of foods. It is clear that retrograded amylose is very resistant to enzymatic hydrolysis *in vitro* but this *in vitro* resistance does not necessarily predict behaviour in the gastrointestinal tract (see Chapter 4).